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Green Synthesis of ZnO Nanostructures using Different Fruit Extracts

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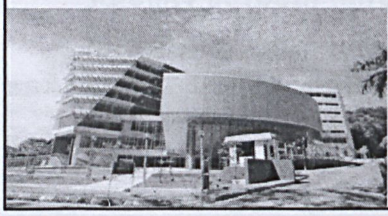

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INTRODUCTION

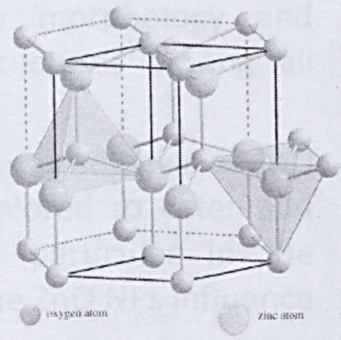
Zinc oxide, ZnO

- One of the most studied multifunctional material due to its unique physical and chemical properties
- found in the in the earth's crust as mineral zincite however commercially used ZnO is prepared synthetically

INTRODUCTION

Zinc oxide, ZnO

- a white solid and is generally insoluble in water
- exists as hexagonal wurzite structure at room temperature
- has high thermal and mechanical stability at room temperature
- has strong room temperature luminescence, good transparency



INTRODUCTION

Zinc oxide, ZnO

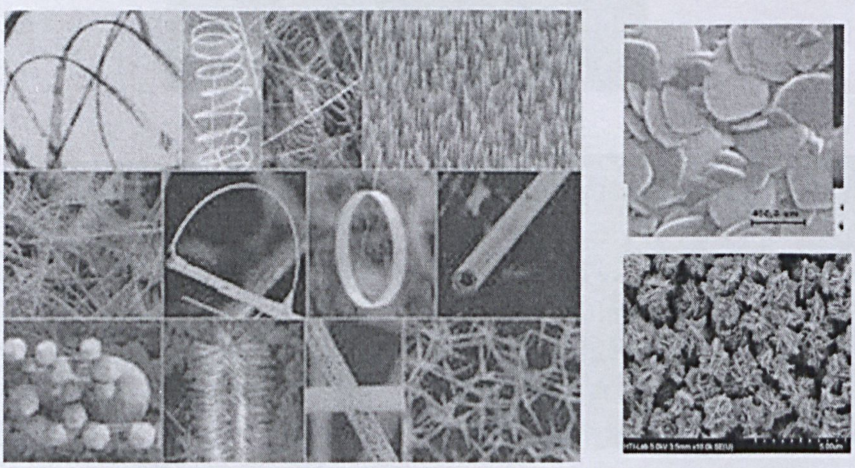
- a semiconductor material with a direct wide band gap energy (3.37 eV)
- has unique optical and chemical behaviours which can easily tuned by changing the morphology, thus an attractive candidate for many applications such as UV lasers, light-emitting diodes, solar cells, gas sensors, photodetectors and photocatalysts.
- has low toxicity, biocompatibility and biodegradability, making make it a material of interest for biomedicine and in pro-ecological systems

INTRODUCTION

Structure and Morphology of Zinc oxide

- has great variations in structure morphology and probably the richest family of structures among all materials
- numerous shapes, dimensions and morphologies of ZnO structures of have been widely explored to cater and improve different applications (in particular in the nanoscale as the shape and size of the ZnO NPs influence their physical properties)

INTRODUCTION



1D - nanorods, nanobelts, nanospring, nanorings, nanohelix, nanowires, nanocages, nanotubes: 2D – nanoplate/sheet: 3D - urchin-like, flower, snowflake, etc

Different morphologies of ZnO nanostructures (Wang, 2004, Copyright 2004 by Elsevier Ltd)

SYNTHESIS OF ZnO

Physical
Chemical
Biological

→

Nanomaterials with specific sizes/shapes

SYNTHETIC METHODS

Physical Approach

Mechanical method

1) High energy ball milling
2) Melt mixing

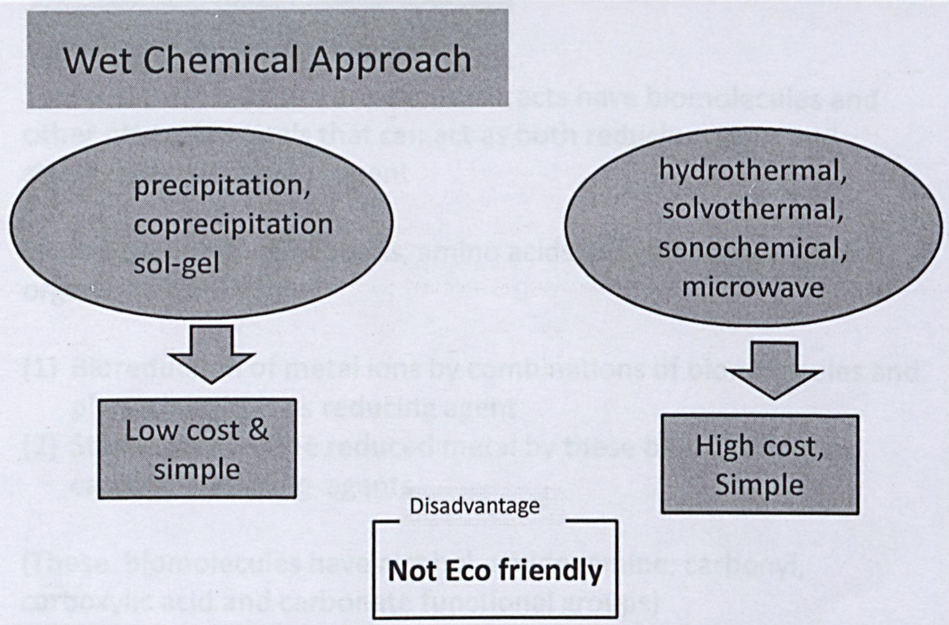
Vapour / evaporation method

1) Physical vapor deposition
2) Laser Ablation
3) Sputter deposition
4) Electric arc deposition

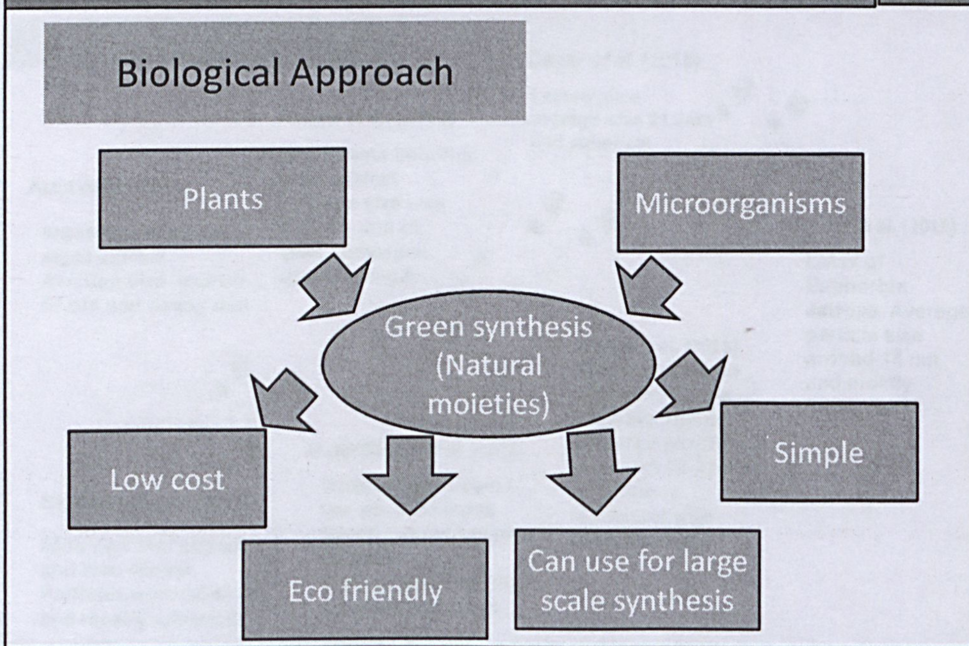
Disadvantage

1) Expensive (costly equipment)
2) Slow
3) Cannot employ on large scale

SYNTHETIC METHODS



SYNTHETIC METHODS



SYNTHETIC METHODS

Biological Approach

These natural moieties and plant extracts have biomolecules and other phytochemicals that can act as both reducing agent and stabilization or capping agent

Examples: enzymes/proteins, amino acids, polysaccharides and organic acids/vitamins

(1) Bioreduction of metal ions by combinations of biomolecules and phytochemicals as reducing agent
(2) Stabilisation of the reduced metal by these biomolecules as capping/stabilsing agents

(These biomolecules have alcohol, amide, amine, carbonyl, carboxylic acid and carbonate functional groups)

LITERATURE REVIEW

Green synthesis of ZnO

Sangeetha et *al.* (2011)
Aloe vera leaf extract and zinc nitrate
Particles were 25 45 nm and mostly spherical

Azizi *et al.* (2014)
argassum muticum algae extract
Average size was 30-57 nm and hexagonal

Abdul Salam *et al.* (2014)
Ocimum basilicum L. var. purpurascens Benth-Lamiaceae leaf extract.
Particle size was 50 nm and hexagonal

***Thema* et *al.* (2015)**
Agathosma betulina plant extract
Average size was 15.8 nm and of quasi-spherical agglomerated

***Ramesh al.* (2015)**
Solanum nigrum leaf extract as a capping agents
Average particle size was 20-30 nm and nearly spherical with rough surface.

Davar *et al.* (2015)
Lemon juice
average size 21.5nm and spherical

***Geetha* et *al.* (2016)**
Latex of Euphorbia Jatropa. Average particle size around 15 nm and mostly hexagonal

OBJECTIVES

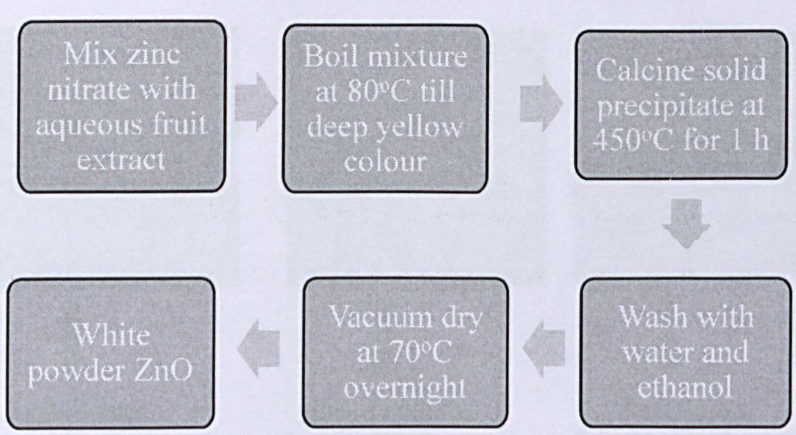
To prepare **ZnO nanostructures** by **green synthesis** method

(i) zinc nitrate hexahydrate as its precursor
(ii) fruit extracts

- Source of fruit extract is known to influence the characteristics of the nanoparticles (Kumar & Yadav, 2009).
- Different fruit extracts contain different concentrations and combinations of phytochemicals - organic reducing and stabilising agents (Mukunthan & Balaji, 2012).

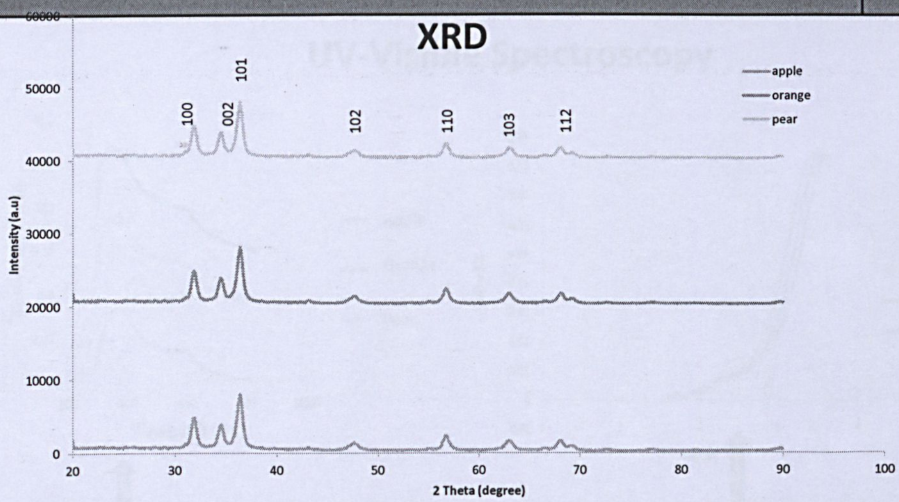
METHODOLOGY

Synthesis of ZnO



RESULTS

XRD

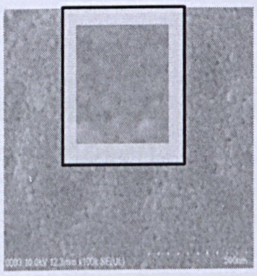


From XRD pattern
- confirms formation of ZnO which shows crystallinity
- diffraction peaks corresponds to hexagonal wurtzite structure
- high phase purity of the ZnO

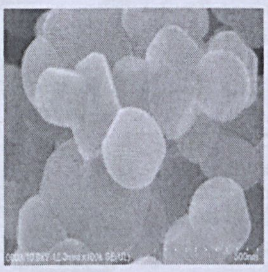
Average crystallite size around 10 nm

RESULTS

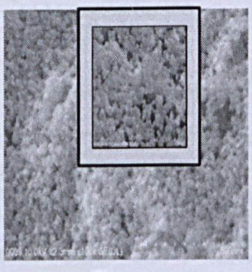
FESEM



Apple extract. Spherical-like structure with particle size range of 40-50 nm



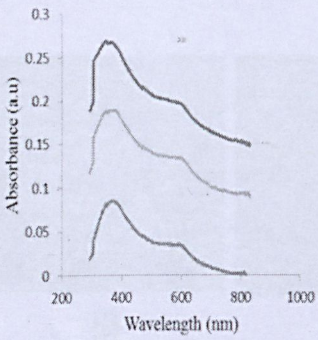
Orange extract. Hexagon like structure, size of particle range from 300-350 nm

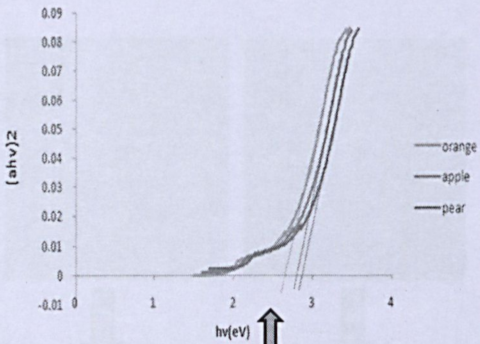


Pear extract. Spherical like structure with particle size range of 40-50 nm

RESULTS

UV-Visible Spectroscopy





absorption peak at 360 nm - characteristic band for pure ZnO

direct optical energy band gap was found to be 2.7-2.8 eV

RESULTS

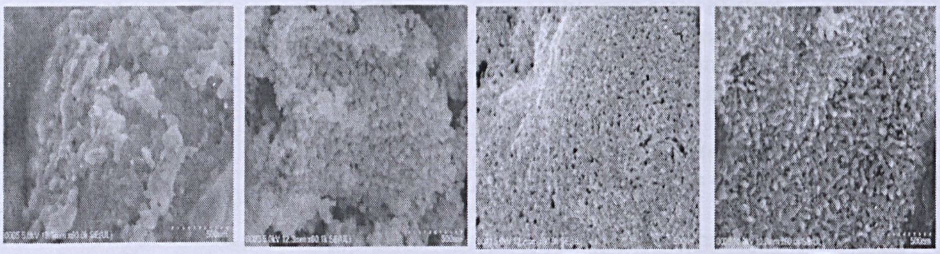
Effect of pH

Pear extract was chosen

1. Synthesis of ZnO nanoparticles from apple extract has been reported
2. ZnO synthesized from orange extract shows larger particle size range of 300-350 nm
3. ZnO from pear extract give particle size in the range 40-50 nm

RESULTS

FESEM



irregular structure at pH 2

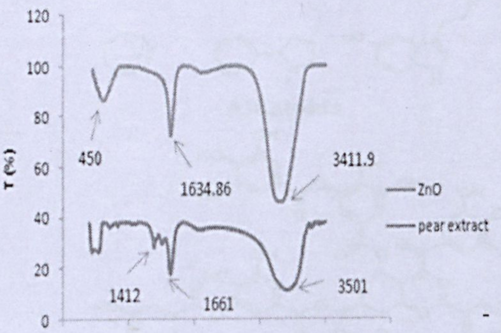
Non-spherical structure at the pH 4

uniform spherical-like structure at pH 7

rice-like structure at pH 11

RESULTS

FTIR Spectroscopy



ZnO

1634.86 cm^{-1} → **Zn-O stretching**

450 cm^{-1} → **Zn-O deformation**

3411.90 cm^{-1} → **O-H stretching**

P ear extract

- many peaks reflecting the complex organic functional groups present

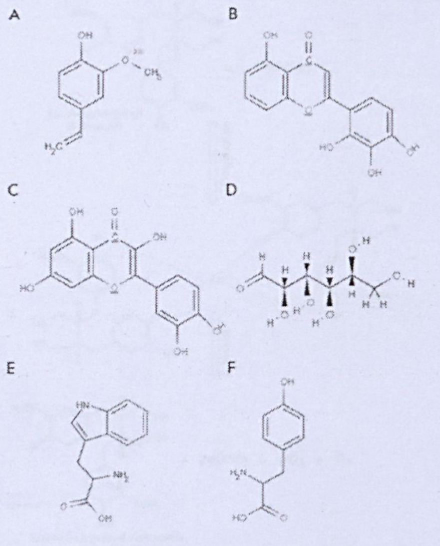
3501 cm^{-1} → **–OH group**

1412 cm^{-1} → **(NH)C=O group**

1661 cm^{-1} → **sp^2 C=C and C=O bond**

RESULTS

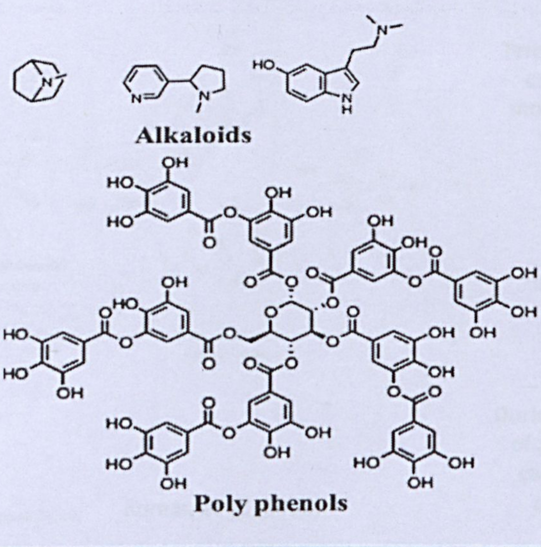
Plant metabolites



The main types of plant metabolites involved in the synthesis of metal nanoparticles (acting as reducing and stabilising agents:
A – terpenoids (eugenol);
B,C – flavonoids (luteolin, quertcetin);
D – a reducing hexose with the open chain form;
E,F – amino acids

RESULTS

Plant metabolites



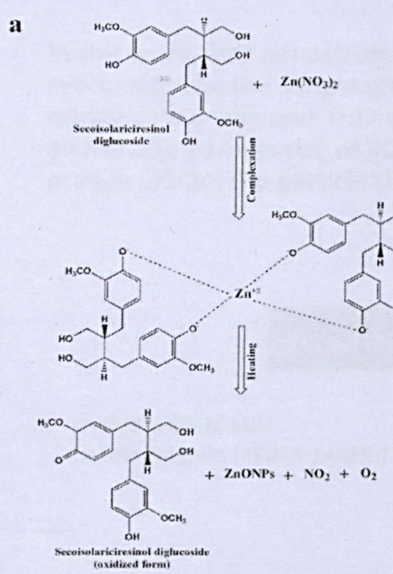
Alkaloids

Polyphenols

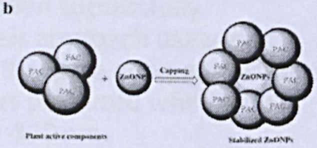
RESULTS

Proposed mechanism of nanostructures formation

a



b



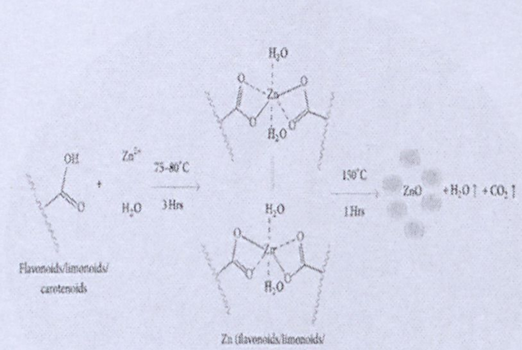
Probable mechanism :

a) complexation and reduction of zinc ions by phytochemicals (secoisolariciresinol diglucoside)
b) stabilization of biosynthesized ZnO NPs by capping with plant active compounds (PAC).

Abbasi et al (2017).

RESULTS

Proposed mechanism of ZnO formation



Extract coated ZnO-NPs

Terpenoids/flavonoids/limonois/ carotenoid/reducing hexose molecules have free OH/COOH, which can react with Zn^{2+}

form zinc flavonoids/ limonoids/carotenoid complex

During drying process, conversion of zinc flavonoids /limonoids / carotenoid complex into ZnO nanoparticles takes place.

Kumar, et al. (2011)

CONCLUSION

- In this work, ZnO nanostructures have been successfully synthesized by the simple green synthesis approach using zinc nitrate precursors and fruit extracts. With apple and pear extracts, an average particle size of 40 -50 nm was produced while with orange extract the particle size was 300-350 nm.

Acknowledgements

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